

# Development of Photodegradable Environment Friendly Polypropylene Films

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## Abstract

In order to minimize the environmental pollution due to littered plastic packaging polypropylene (PP) films, the photodegradation of PP films was carried out under natural weathering conditions using ferric carboxylates as prodegradants. Since sunlight (energy source for the photodegradation) is abundantly available, photodegradation has been chosen one among the various degradation technologies. The photodegradation was followed using the simplest analytical techniques like Fourier Transform Infrared Spectroscopy, mechanical properties measurements and scanning electron microscopy. All the ferric carboxylates used as prodegradants have a strong influence on the photodegradation behaviour of PP and facilitate the UV induced photooxidative degradation. The effectiveness of the prodegradants in accelerating the PP photodegradation was of the order of ferric caprate > ferric laurate > ferric myristate > ferric palmitate > ferric stearate. The plots of days of exposure required to reach a certain carbonyl index value such as 0.2-0.3, 0.4-0.5, 0.6-0.7, 0.8-0.9 and 1.0-1.1 and the  $t_{1/2}$  parameter obtained from the elongation at break percentages versus number of carbon atoms presented in the alkyl part of the prodegradants added showed that the rate of UV induced photooxidative degradation of PP is linearly related to the number of carbon atoms presented in the alkyl part of the added ferric carboxylates. Moreover, the increase in the concentration of Fe (III) ion in the PP films plays an important role in the photodegradation and accelerates PP degradation. The results also showed that the PP and PP containing 0.2% of ferric carboxylates degraded faster in the summer season than that in the winter season. This effect is due to the influence of the average weathering parameters mainly outdoor temperature.

## Keywords

*Polypropylene; Ferric carboxylates; Natural weathering; FTIR; SEM*

## Introduction

Plastic shopping bags have nowadays become an integral part of our daily life and so their consumption increases due to their low cost and less weight. It is being discarded by uncaring persons leading to environmental pollution worldwide thereby decreasing the landfill capacity for plastic disposal and slow degradation of plastic litter in the environment. It leads to generating intense interest in degradable plastics in the last quarter century. Polyolefins are one of the important materials for packaging applications because of their combination of flexibility, toughness, excellent barrier properties and also inertness towards outside factors like heat, radiation, chemicals and micro organism.

Among the polyolefins, nowadays polypropylene is one of the most widely used among all the commodity polymers. The versatility of this material arises from the cheap petrochemical stocks as raw materials, the sophisticated and efficient catalytic polymerization processes and the ease of the processing of the final polymer as a fabricated article by injection moulding or as textile by spinning or as film by blown extrusion. With increased production, PP film has been used extensively for food contact applications, due to its higher melting point, low water absorption tendency and aroma retention capacity. Thus, its consumption increased and caused littering which led to environmental pollution.

Recently, the more challenging and interesting field of developing degradable polymers for packaging and disposals to minimize litter has resulted in the availability of several commercialized products. Khare et al. and Chouzouri et al. made investigation towards development of eco-friendly plastics using bio-active fillers. However, presently the most available

commercial polymer such as poly-propylene is not responsive to biodegradation by bacteria, fungi, yeasts or enzymes; photodegradation, photooxidation and autooxidation are the main pathways for their degradation. Photooxidation leads to an increase in the low molecular weight fractions by chain scission, thereby facilitating biodegradation. In addition to the freely and abundantly available sunlight as energy source for degradation, the development of photodegradable polypropylene is the theme of the present investigation. The prior art methods to develop photodegradable plastics are to synthesize a polymer comprising carbonyl groups in its main chain or its pendent side chain, blending degradable polymer with a non-degradable polymer or incorporating a photo-degradation promoting agent (prodegradant) into a polymer. This present investigation is focused on the incorporation of photodegradation promoting additives into PP. The additives normally used for the initiation of degradation are aromatic ketones, dithio carbamate, acetyl acetonates, organo soluble transition metal ions, etc., which can act as thermal and/or photooxidant for the polymer. However, a more convenient and the simplest method of blending non-toxic ferric carboxylates such as ferric caprate (MF03), ferric laurate (MF04), ferric myristate (MF05), ferric palmitate (MF06) and ferric stearate (MF07) with polypropylene on the enhancement of photodegradability of PP is involved in this present study.

Literature survey indicated that till date, no work on the use of non-toxic transition metal carboxylates as prodegradant to enhance the photodegradability of PP under natural weathering conditions has been reported. However, several authors have made a detailed work on the photodegradability of PE using various transition metal carboxylates as prodegradant both under natural and artificial weathering. For example, the effect of a series of transition metal (Ti, V, Mn, Fe, Co, Ni, Cu, and Zn) stearates on the photodegradation of a high density polyethylene was studied by Osawa et al.. The author reported that iron stearate is more effective at an early stage of photodegradation, vanadium and manganese stearates accelerate while copper stearate retards it. Other stearates show no appreciable effect on the photodegradation.

The photodegradability of low density polyethylene using cerium (III) and cerium (IV) stearate as the prodegradant was extensively studied by Havnden. The author found that cerium (III) was effective in promoting both photo- and thermo-oxidation of LDPE,

with effectiveness increasing with concentration. But, cerium (IV) was less effective in promoting photo-oxidation. Eyenga et al. have compared the photocatalytic activity of 1, 2-dihydro-2, 2, 4-trimethyl quinolene (OTMQ) with commercially available ferric stearate in the UV ageing of polyethylene and polypropylene films and the results concluded that ferric stearate was much more efficient than OTMQ. Sheikh et al. made an investigation to develop an environmentally degradable polymer material. A masterbatch prooxidant system containing oleic acid, benzoyl peroxide and ferric stearate was blended into low density polyethylene and the prepared films were subjected to both natural and artificial weathering. The authors showed that the presence of incorporated prooxidants played an important role in enhancing the degradation process of polyethylene. Roy et al. has reported the effect of chain length of cobalt carboxylates namely laurate, palmitate and stearate on the photodegradation behaviour of low density polyethylene. The author concluded that all the above mentioned cobalt carboxylates promote photodegradation but the order of photodegradation was stearate > palmitate > laurate.

In general, the degradation rate of plastics depends on the weathering conditions including sunlight, temperature, rain, humidity, pollutants, thermal cycles and oxygen content. All these parameters may vary from region to region and place to place and have also shown significant seasonal variations. Thus, its damage degree depends on the nature, the way and the extension of the interaction of the material with surrounding atmosphere. Therefore, the complex weather factors influence the polymer and results in irreversible changes in the chemical structures and in the mechanical properties which reflect in the lifetime of the material. Hence, the present study involves the photodegradation of PP films under natural weathering conditions in two different seasons to predict the effects of ferric carboxylates (prodegradants) and weathering parameters on the photodegradability of PP.

## Experimental Procedure

Polypropylene (Repol grade H100EY) obtained from Reliance Industrial Ltd. (Jamnagar, India) is the material chosen for the present investigation. This material contains Irganox antioxidant (500-1000 ppm). The physical properties of the PP material were listed. To synthesize prodegradants (iron salts of various fatty acids), potassium hydroxide pellets and ferric sulphate monohydrate purchased from Merck, Mumbai, India and decanoic acid (capric acid),

dodecanoic acid (lauric acid), tetradecanoic acid (myristic acid), palmitic acid and stearic acid supplied by Alfa Aesar Johnson Matthey GMBH, Karlsruhe,

Germany were used as such without further purification.

TABLE 1 AVERAGE VALUES OF WEATHERING PARAMETERS MEASURED DURING NATURAL WEATHERING OF PP AND PP CONTAINING FERRIC CARBOXYLATES.

Natural Weathering	T (°C)	P (mmHg)	Intensity		Humidity % rel	Rainfall (cm)
			UV (x 1μW/cm <sup>2</sup> )	Light (x 100LUX)		
Winter (Dec' 06 – Mar' 07)	34	748	998	937	40	3.5
Summer (May 07 – July 07)	39	745	325	726	39	2.5

According to the procedure reported in the literature, iron salts of capric acid, lauric acid, myristic acid, palmitic acid and stearic acid were synthesized by reacting ferric sulphate monohydrate with corresponding potassium salt of fatty acid. The salts prepared are ferric caprate (MF03), ferric laurate (MF04), ferric myristate (MF05), ferric palmitate (MF06) and ferric stearate (MF07).

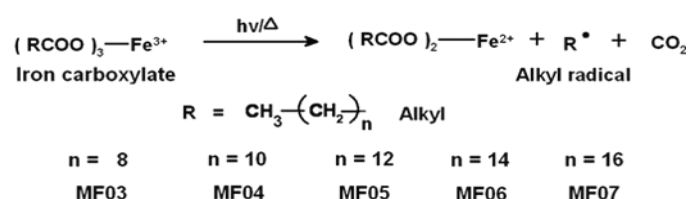
The virgin polypropylene was taken in 4 kg batches and blended with 0.2% of prodegradants (MF03, MF04, MF05, MF06 and MF07) prepared using a blender made by Modern Plastic Industries (Coimbatore, India). The virgin polypropylene and the various prodegradants blended polypropylene were extruded blown into films using an extruder (Model PP-750) made by Klockner Windsor India Ltd., (Thane, Mumbai, India). During extrusion the three barrel zones were kept at 200°C, the die was maintained at 175°C and the screw revolution was maintained at 200 rpm. The films were obtained with the width of 36 cm and a thickness of 62 μm. The extruder was cleaned by running 4 kg of virgin PP material before the addition of every new material.

The extruded films of virgin PP and PP containing 0.2% of prodegradants (MF03, MF04, MF05, MF06 and MF07) were exposed to natural weathering on suitably designed and fabricated outdoor exposure racks made by Star Engineering Works, Thiruthangal, Tamil Nadu, India according to the specification of the ASTM 1435 standard. The racks are placed at an angle of 45° to the ground and facing towards south. Each rack has 12 segments, in which each segment has four subdivisions. In three of these racks, each segment has the dimension of 58.5 × 41.5 cm<sup>2</sup> (a × b) and each subdivision has a dimension 26 × 17.5 cm<sup>2</sup> (c × d). In another one, each segment has the dimension of 43.5 × 31 cm<sup>2</sup> (a × b) and each subdivision with 13.5 × 12.5 cm<sup>2</sup> (c × d). The sectional view of a single segment is found elsewhere.

The outdoor exposure racks were located in the Kamaraj College of Engineering and Technology, S.P.G.C. Nagar, K.Vellakulam Post 625 701, Virudhunagar, Tamil Nadu, India located at a latitude of 9.36° N and longitude of 77.58° E and situated near Madurai in the southern part of Tamil Nadu, India. The average annual rainfall is 60 - 80 cm and the annual average temperature is around 27.5°C.

To predict the optimum quantity of prodegradant to be used for the natural weathering of PP, PP films containing varying concentrations (0.2, 0.4 and 0.6%) of ferric stearate were weathered during the period from 22.09.2005 to 09.12.2005. The measured average temperature, pressure and humidity were 35°C, 747 mm Hg and 53 % rel., respectively. The average visible and UV light intensity were 741 × 10<sup>2</sup> LUX and 361 μW/cm<sup>2</sup>. The photodegradation of PP films was followed for each and every day by recording the FTIR spectrum of the weathered PP films.

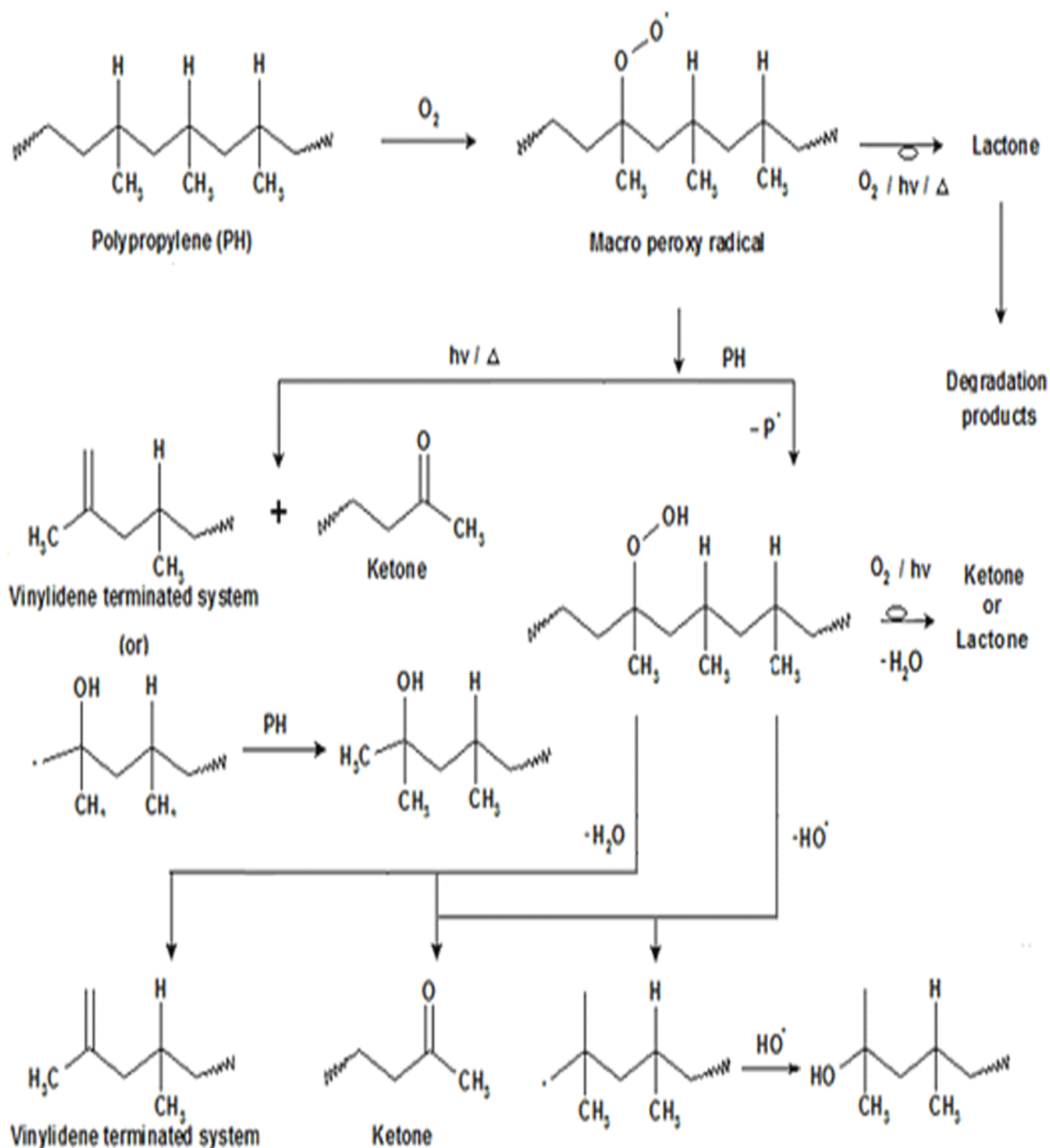
The role of ferric carboxylates (MF03, MF04, MF05, MF06 and MF07) and weathering parameters on the photodegradation of the PP was also studied by subjecting the material to natural weathering during the periods, December 2006 to March 2007 (winter season) and May 2007 to July 2007 (summer season). The sampling was done at regular time intervals and the naturally weathered samples were characterized using FTIR, UTM and SEM analysis.



SCHEME 1 INITIATION REACTION OF IRON CARBOXYLATES TOWARDS POLYMER DEGRADATION

The outdoor temperature was measured using Jennson Research-GRD glass thermometer. Pressure was measured using Besto Barometer (640–810 mm Hg). Huger Hygrometer (85 mm) model 3123 was employed to measure the humidity. The intensity of UV light was

measured by Lutron UV-340 UV Light meter 0–1999 ( $\times 1 \mu\text{W}/\text{cm}^2$ ) model D 44197. LUTRON LX-101 model (CE 35187) 20000–50000 ( $\times 100 \text{ LUX}$ ) was used to measure the visible light intensity. All



SCHEME 2 FORMATION, INTRA AND INTER-CHAIN HYDROGEN ABSTRACTION OF PEROXY MACRO RADICALS

the weathering parameters were measured during 12.00 h to 13.00 h of the day and the average values are presented in TABLE 1.

Fourier transform infrared spectrophotometer (FTIR) is an important tool to predict the structural changes occurring in the material during photodegradation. The FTIR spectra of the non-weathered and weathered virgin PP and PP containing prodegradants (0.2%) were recorded on a FTIR-8400S Spectrophotometer which was supplied by SHIMADZU (Tokyo, Japan). FTIR spectra of all the samples were recorded using 20 scans with  $4\text{ cm}^{-1}$  resolution. The FTIR spectra of weathered PP revealed significant changes in the regions of hydroxyl ( $3600\text{--}3200\text{ cm}^{-1}$ ), carbonyl ( $1800\text{--}1700\text{ cm}^{-1}$ ) and unsaturated ( $1000\text{--}800\text{ cm}^{-1}$ ) groups as a function of exposure time under natural weathering. Based on the structural changes, indices of hydroperoxide, hydroxyl, carbonyl, carboxylic acid, ester, lactone and vinylidene were calculated as the ratio of absorbance corresponding to peak maxima of the functional group concerned to the absorbance corresponding to peak maxima of the reference peak. The wavenumber regions followed for the functional groups in the degradation products were listed in our previous paper.

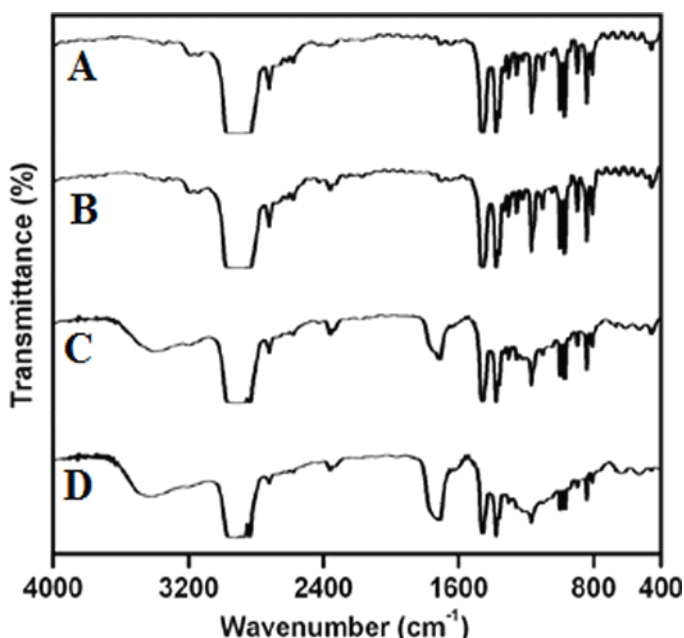
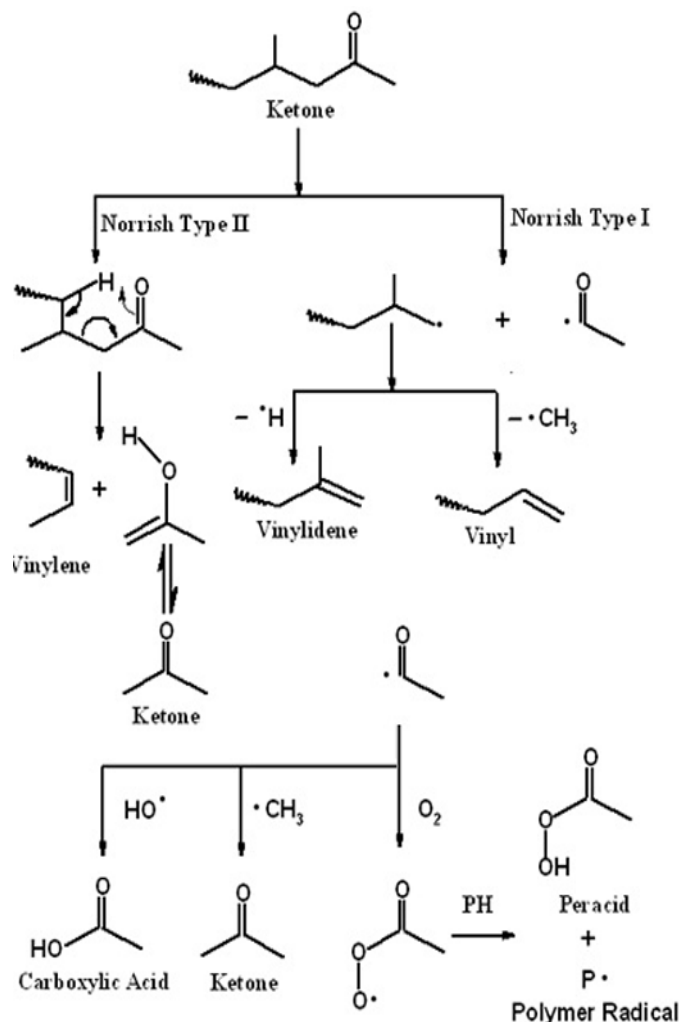


FIG. 1 FTIR SPECTRA OF NATURALLY WEATHERED (3 DAY) PP CONTAINING FERRIC STEARATE IN DIFFERENT PROPORTIONS:

(A) 0% (B) 0.2% (C) 0.4% AND (D) 0.6%.

In literature, the absorbance bands occur at 840, 974, 1166, 1455 and  $2720\text{ cm}^{-1}$  have been considered as reference peaks for polypropylene. In the present work, the peak at  $974\text{ cm}^{-1}$  ( $-\text{CH}_3$  rocking band) was chosen as reference peak, which remained unchanged during degradation.



SCHEME 3 DECOMPOSITION OF KETONE VIA NORRISH TYPE I AND TYPE II REACTION

The mechanical properties like elongation at break (%) and tensile strength of naturally weathered PP film samples were determined using HOUNSFIELD Material Testing Machine (Model S – series, H5K – S), which comprises of a load cell (5 kN) and HT55 ultra light vice grips, supplied by Tinius Olsen Ltd., (Surrey, England). It was operated at a speed of  $150\text{ mm min}^{-1}$  with the grip distance of 80 mm on the film samples. For each sample, four tests were conducted and the average value was chosen for further data analysis.

The morphological change occurring in the surface of naturally weathered PP films was examined using a scanning electron microscope. Sample surfaces were sputtered with gold using usual techniques and then analysed using JEOL (JSM-840A) scanning electron microscope (10 kV) supplied by JEOL Ltd., (Tokyo, Japan). Photo micrographs were captured at a uniform magnification of 500x.



## Results and Discussion

### Photooxidative Degradation Mechanism

The chemical changes occurring in the material during photooxidative process are very complex and it was generally assumed as a free radical chain mechanism. In general, in the absence of photoinitiators, the initiation of polypropylene photooxidation is by the abstraction of hydrogen atom preferably tertiary hydrogen by free radicals produced due to the decomposition of chromophoric impurities such as hydroperoxide formed during processing. The most probable mechanism for the degradation of polypropylene in the presence of photoinitiators like iron carboxylates, is presented in SCHEMES 1-3. In the first step, the iron carboxylates absorb energy in the form of light and heat and undergo decarboxylation liberating alkyl free radicals (SCHEME 1).

In the next step, the produced alkyl free radicals move into the polymer matrix and abstract the labile tertiary hydrogen from polypropylene yielding macro alkyl radicals. These macro alkyl radicals react with atmospheric oxygen and generate macro peroxy radical (SCHEME 2). These macro peroxy radicals are converted into hydroperoxide *via* intramolecular hydrogen abstraction and intermolecular hydrogen

abstraction (SCHEME 2). Due to the less stability of hydroperoxides under light and heat, they decompose into alkoxy and hydroxy radicals. It is an important step since the resultant macro alkoxy radical leads to main chain scission resulting in the formation of ketones. Thus, the generated ketones undergo Norrish Type I and Norrish Type II reactions and liberate different kinds of photooxidation products like aldehydes, carboxylic acids, ester, lactone, peracid, perester etc. which are presented in SCHEME 3.

### FTIR Studies

The FTIR spectra for the three days naturally weathered PP film containing ferric stearate of various proportions (0.2, 0.4 and 0.6%) are presented in FIG. 1. From this FIG., it is clear that three days weathered virgin PP (FIG. 1(A)) and PP containing 0.2% ferric stearate (FIG. 1(B)) showed no characteristic peaks in the carbonyl and hydroxyl region. A strong peak was noted in the carbonyl and hydroxyl group region in the FTIR spectra for the three days weathered PP films containing 0.4% (FIG. 1(C)) and 0.6% (FIG. 1(D)) ferric stearate. This clearly showed that the PP films having 0.4 and 0.6% of ferric stearate have undergone photooxidative degradation which led to the formation of carbonyl and hydroxyl group compounds. Further, it showed that as the days of

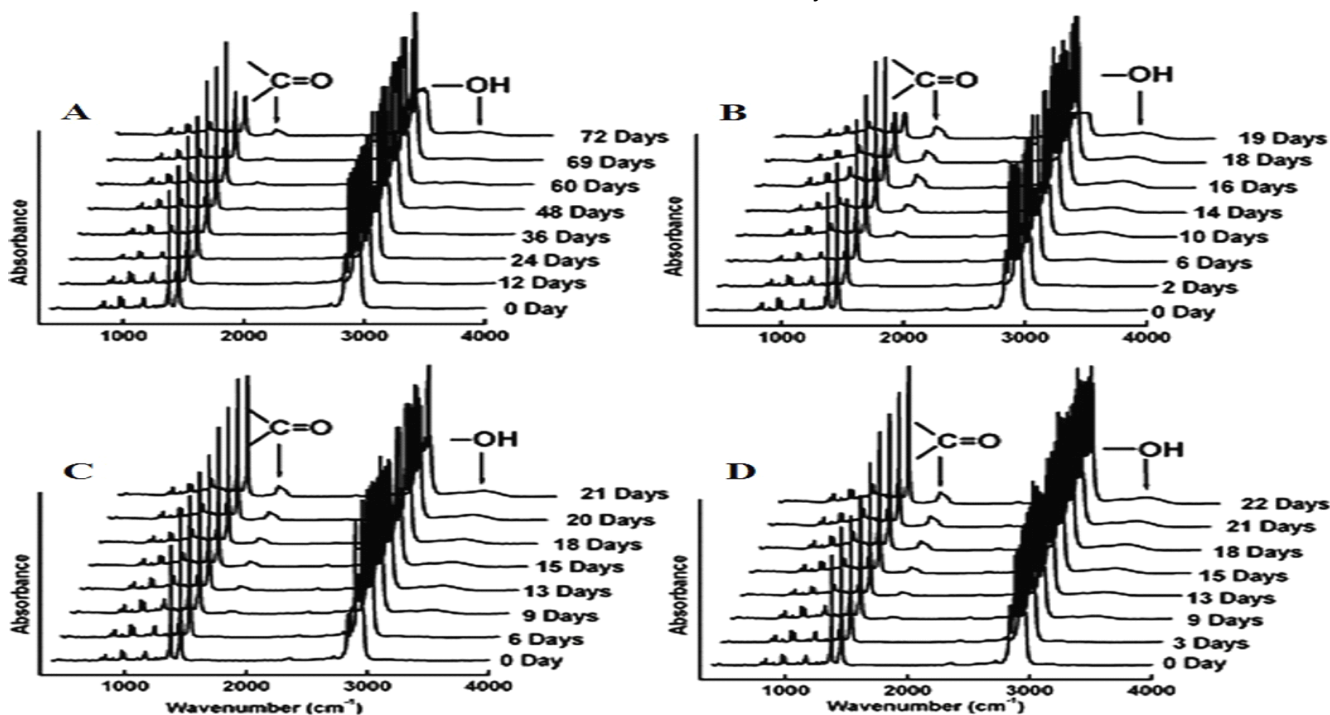


FIG. 2 FTIR SPECTRA OF NATURALLY WEATHERED (SUMMER SEASON) PP AND PP CONTAINING 0.2% OF FERRIC CARBOXYLATES: (A) VIRGIN PP (B) PP:MF04 (C) PP:MF06 AND (D) PP:MF07.

exposure and the level of concentration of prodegradant increased, the quantity of carbonyl and hydroxyl groups in weathered PP increased.

The PP film containing 0.2% of ferric stearate showed the carbonyl and hydroxyl peaks in the FTIR spectrum when the films were weathered for eight days of exposure time. Further, owing to the relatively higher loading of ferric stearate (0.4 % and 0.6%), the photooxidative degradation of PP proceeds faster and the material developed detectable quantities of carbonyl groups within a short duration of exposure i.e., 3 day. Hence, the authors decided to load PP with 0.2% of

various ferric carboxylates (MF03, MF04, MF05, MF06 and MF07) and study the effect of these prodegradants on the photooxidative degradation of polypropylene.

The FTIR spectra for the weathered PP films containing 0.2% of ferric carboxylates during summer season are depicted in FIG. 2. From this figure, one can easily see the progressive increase of both the hydroxyl and carbonyl absorbance as the days of exposure increased. Based on the considerable changes noted in the hydroxyl and carbonyl regions in the FTIR spectra of weathered PP film samples, the hydroperoxide, hydroxyl, lactone,

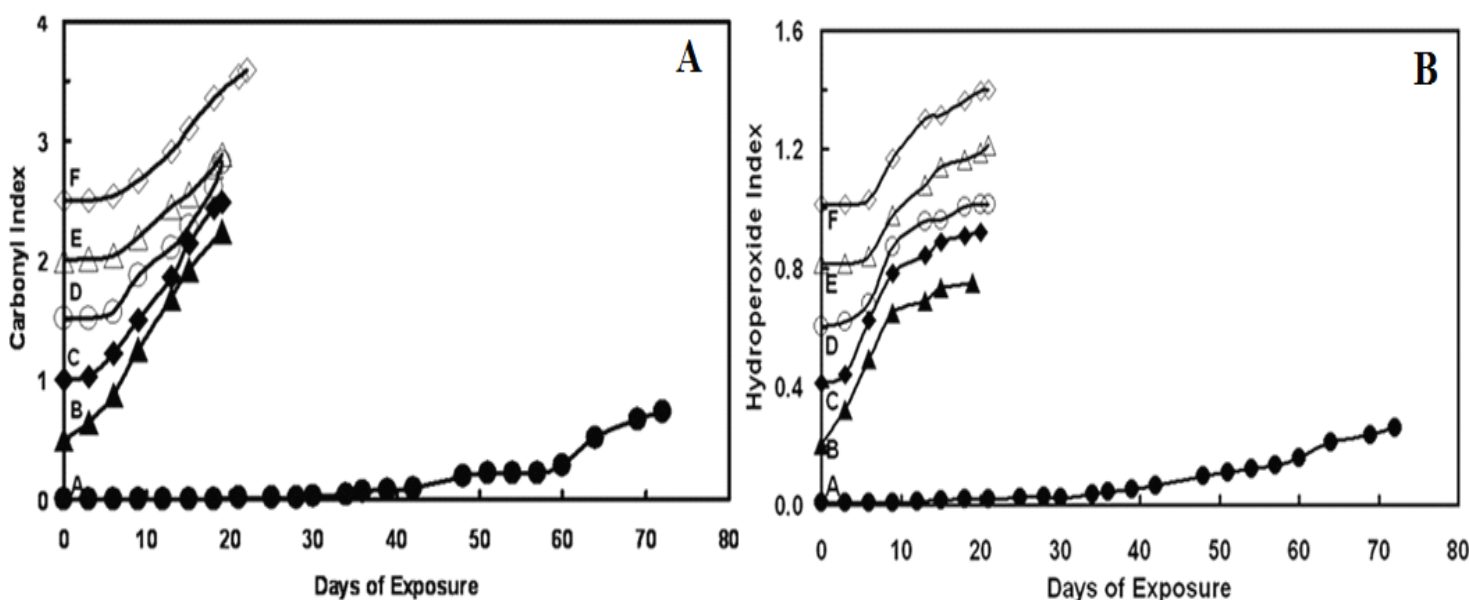


FIG. 3 VARIATION IN CARBONYL INDEX (A) AND VARIATION IN CARBONYL INDEX (B) OF NATURALLY WEATHERED PP AND PP CONTAINING 0.2% OF FERRIC CARBOXYLATES FOR SUMMER SEASON. EXCEPT THE CURVE FOR VIRGIN PP (●), THE CURVES OF PP:MF03 (▲), PP:MF04 (◆), PP:MF05 (○), PP:MF06 (Δ), AND PP:MF07 (◇) ARE SHIFTED ON THE ORDINATE BY THE DISTANCE AB, AC, AD, AE AND AF, RESPECTIVELY.

ester, carbonyl, carboxylic acid and crystallinity index have been calculated.

### Carbonyl Index

The most used parameter, carbonyl index, to evaluate the extent of degradation of PP was calculated using the formula given below and its variations with respect to the days of exposure during natural weathering in summer season are depicted in FIG. 3A. For naturally weathered PP samples, the carbonyl index value increased with increasing exposure period only after certain days of exposure and this period may be considered as the induction period for the photooxidative degradation behaviour. In this time,

physical and morphological changes occurring in the PP samples, which aid the oxygen solubility and facilitate the oxidation reaction. Depending upon the environmental conditions and the nature of the prodegradants added, the induction period varied and so did the degradation rate.

$$\text{Carbonyl Index} = \frac{\text{Absorbance at } 1715 \text{ cm}^{-1}}{\text{Absorbance at } 974 \text{ cm}^{-1}}$$

From previous studies, it is clear that the induction period for the photooxidative degradation of virgin PP during natural weathering (winter season) is around 50 day. Whereas all PP samples having prodegradants showed prominent increase in the carbonyl index values

within 20 days of exposure. However, in the case of virgin PP films weathered during summer season (FIG. 3), the carbonyl index value increased after an exposure period of 45 day. All prodegradants containing PP samples showed prominent increase in the carbonyl index value within 10-15 days of exposure. This clearly indicates that the incorporation of the ferric carboxylates in PP speeds up the photooxidative degradation during natural weathering and the effect being controlled and influenced by the average weathering parameters (TABLE 1). Eventhough the average values of UV and visible light intensity were low during summer season when compared to winter season (TABLE 1), PP weathered during summer degraded in a faster rate. This observation reveals that the outdoor temperature is the key factor that dictates the degradation rate. The secondary factors like relative humidity, UV intensity, visible light intensity and rainfall also exercise influence on the photodegradation process.

Thus, degradation process in the natural environment was complex due to the presence of sunlight, wind, rain and non-isothermal conditions. The main effect of the rising temperature on the degradation process was related to the enhanced mobility of radicals for reactions and therefore the increased in the rate of degradation process. Sheikh et al., Rajakumar et al., and Gonzalez et al. have also pointed out that the environmental temperature seems to be the key factor that influences more on the rate degradation of polyolefins.

From FIG. 4, it is clear that the total number of carbon atoms present in the alkyl chain of the iron carboxylate used as the prodegradant for PP plays an important role in the determination of the degradation rate of PP under natural environmental conditions.

As the number of carbon atoms in the alkyl group increased, the induction period for the initiation of the photodegradation of PP increased indicating the mobility of the alkyl radical produced by the decomposition of the iron carboxylate played a substantial role in the photodegradation of PP.

Recently, Roy et al. investigated the photooxidative degradation of LDPE using cobalt carboxylates as prodegradants. The photooxidation was conducted in an artificial weathering chamber. The authors concluded that the rate of photo-degradation increased as the length of the alkyl chain presented in the cobalt carboxylate increased. This result was attributed to the

fact that as the alkyl chain length increased, the carboxylate was capable of blending easily with the base polymer resulting in its increased capability to act as prooxidant.

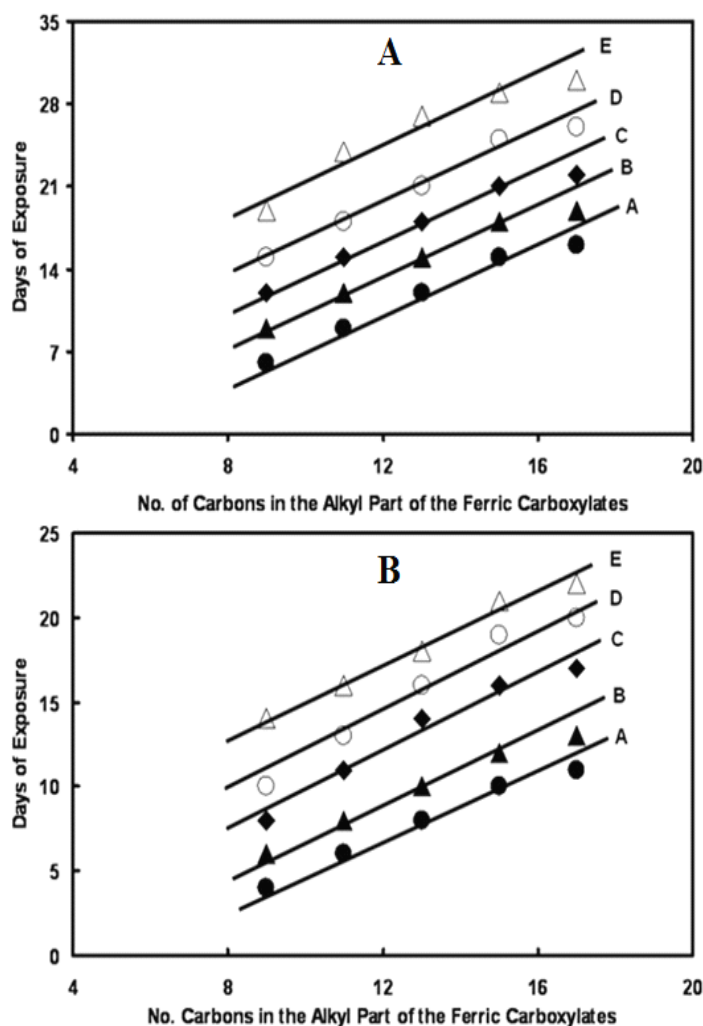


FIG. 4 EXPOSURE DAYS REQUIRED BY PP CONTAINING 0.2% OF FERRIC CARBOXYLATES TO REACH CERTAIN VALUE OF CARBONYL INDEX (A) 0.2 – 0.3 (B) 0.4 – 0.5 (C) 0.6 – 0.7 (D) 0.8 – 0.9 and (E) 1.0 – 1.1 AS A FUNCTION OF NUMBER OF CARBON ATOMS IN THE ALKYL PART OF THE FERRIC CARBOXYLATES DURING NATURAL WEATHERING: (a) WINTER SEASON AND (b) SUMMER SEASON.

A plot of exposure days required to reach a certain carbonyl index value such as 0.2-0.3, 0.4-0.5, 0.6-0.7, 0.8-0.9 and 1.0-1.1 *versus* number of carbon atoms in the alkyl part of ferric carboxylates is presented in FIG. 4. From this figure, one can observe almost a linear trend for all carbonyl index value regions which indicates that as the number of carbon atoms in the alkyl part of the ferric carboxylates increased, the exposure time necessary to reach the particular carbonyl index value increased. Moreover, the concentration of Fe (III) ion in the various ferric carboxylates calculated (TABLE 2)



decreased as the number of carbon atoms in the alkyl part of the ferric carboxylate increased and hence the time required for the considerable degradation of PP films is

TABLE 2 CONCENTRATION OF FE (III) ION CALCULATED IN THE VARIOUS PRODEGRADANTS.		
Name of the prodegradant	No. of carbons in the alkyl part of the prodegradant*	Fe(III) ion Concentration
Ferric caprate	9	0.0196
Ferric laurate	11	0.0171
Ferric myristate	13	0.0152
Ferric palmitate	15	0.0136
Ferric stearate	17	0.0123

decreased. This result revealed that the concentration of Fe (III) ion in the ferric carboxylates incorporated with the PP films play an important role for the acceleration of PP degradation and has a direct linear trend to the speed of degradation of PP while a reverse trend (FIG. 5) has been observed to the number of carbon atoms present in the alkyl part of the ferric carboxylates (FIG. 4).

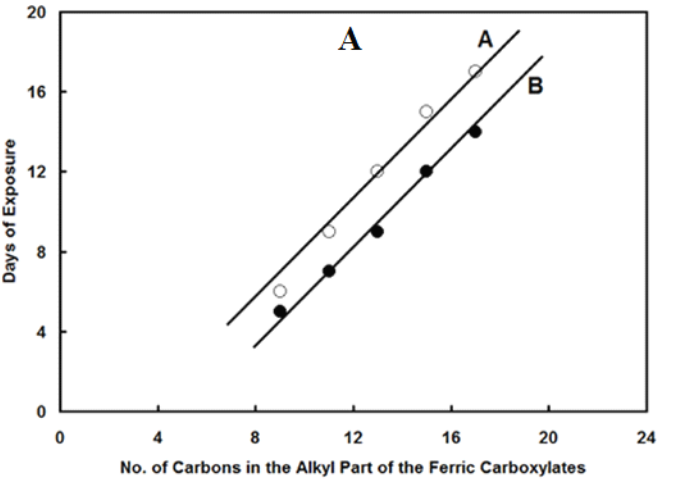


FIG. 6 EXPOSURE DAYS REQUIRED FOR PP CONTAINING 0.2% OF FERRIC CARBOXYLATES TO REACH CERTAIN VALUE OF HYDROPEROXIDE INDEX (0.2 – 0.3) (a): As A Function Of Number Of Carbon Atoms In The Alkyl Part Of The Ferric Carboxylates And (b): AS A FUNCTION OF CONCENTRATION OF FE(III) ION DURING NATURAL WEATHERING: (A) Winter Season And (B) Summer Season

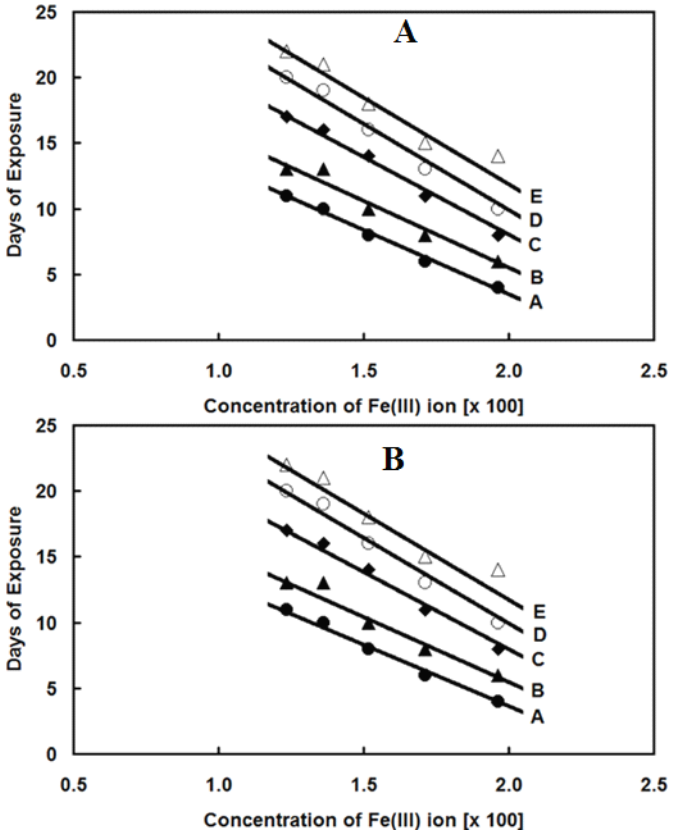


FIG. 5 EXPOSURE DAYS REQUIRED BY PP CONTAINING 0.2% OF FERRIC CARBOXYLATES TO REACH CERTAIN VALUE OF CARBONYL INDEX (A) 0.2 – 0.3 (B) 0.4 – 0.5 (C) 0.6 – 0.7 (D) 0.8 – 0.9 AND (E) 1.0 – 1.1 AS A FUNCTION OF CONCENTRATION OF FE(III) ION IN THE FERRIC CARBOXYLATES DURING NATURAL WEATHERING: (a) WINTER SEASON AND (b) SUMMER SEASON.

Further, this figure showed that the curves of all carbonyl index regions showed almost gradual parallel shift indicating PP, whether it is virgin PP or prodegradant blended PP, during natural

weathering degraded without much change in the degradation mechanism.

The FTIR spectrum of weathered PP showed a broad peak in the carbonyl region ( $1800 - 1700 \text{ cm}^{-1}$ ), and is due to the overlap of different degradation products like lactone, ester, ketone, carboxylic acid etc. The various indices of ketone, lactone, ester and carboxylic acid were calculated as the ratio of absorbance corresponding to peak maxima of the functional group concerned to the absorbance corresponding to peak maxima of the reference peak ( $974 \text{ cm}^{-1}$ ). It is clear that all the indices calculated start to increase steeply in a manner similar to the carbonyl index whether it is virgin PP or PP containing different prodegradants. In short, the induction period noted for the formation of different compounds having carbonyl groups are nearly the same.

In all the samples, carboxylic acid index is having the highest value and is followed by the ketone, ester and lactone indices. Carboxylic acid is a stable degradation product and it is the precursor for the lactone formation. Further, the results showed that the trend noted for weathered virgin PP was similar to the trend noted for the weathered PP having different prodegradants. But the rate of increase of these indices was different and was dependent on the nature of the prodegradant added. All the above observations clearly exemplify the fact that the addition of prodegradants is not altering much the degradation mechanism but is having a definite influence on the rate of photooxidative degradation of PP during the natural weathering. Gallo et al. reported a similar trend in their natural weathering study of polypropylene without any prodegradants, at Messina, Italy but the absorbance values were different and this might be attributed to the nature of the material

investigated and the different climatic condition that was prevailing at the chosen locations.

### Hydroperoxide Index

Hydroperoxide is the first product formed during oxidative degradation of polypropylene and hence it is important to be measured. However, hydroperoxides are rather unstable and hence usually they decompose and form carbonyl compounds, which accumulate as the oxidation process continues. Hydroperoxide concentration was used as one of the indicators for the extent of degradation with respect to exposure time. Hydroperoxide group formation and its decomposition in the course of natural weathering are important aspects that may provide clue regarding the rate of oxidative degradation of materials. The hydroperoxide index was calculated using the following formula,

$$\text{Hydroperoxide Index} = \frac{\text{Absorbance at } 3445 \text{ cm}^{-1}}{\text{Absorbance at } 974 \text{ cm}^{-1}}$$

The hydroperoxide index variation as a function of exposure days are depicted in Figure 3B. From Figure 3B, it is clearly seen that the steep increase of hydroperoxide group and carbonyl group occur in the same time span during natural weathering. So, the unstable hydroperoxide formation and its decomposition leading to carbonyl groups are occurring simultaneously during the photodegradation of virgin PP and PP containing iron carboxylate prodegradants.

Moreover, the time taken to reach hydroperoxide index value of 0.2 to 0.3 has been calculated and is plotted against the number of carbon atoms in the alkyl part of the added prodegradants (FIG. 6). Almost a linear trend is noted for the investigated materials.

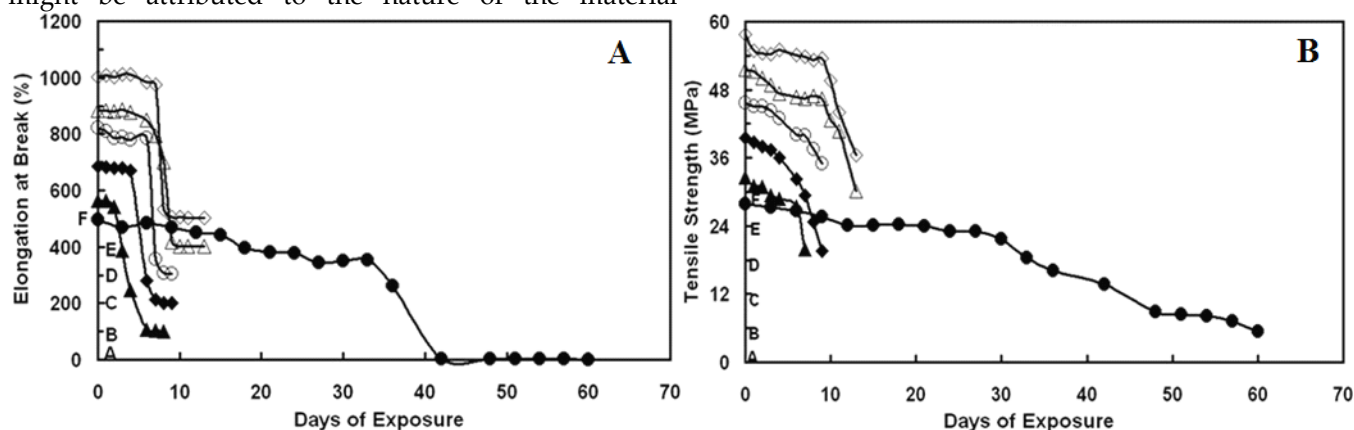


FIG. 7 Variation in elongation at break (%) and variation in tensile strength of naturally weathered PP and PP containing 0.2% of ferric carboxylates for summer season. Except the curve for virgin PP (●), the curves of PP:MF03 (▲), PP:MF04 (◆), PP:MF05 (○), PP:MF06 (Δ), and PP:MF07 (◇) are shifted on the ordinate by the distance AB, AC, AD, AE and AF, respectively.

It is clear that the weathering conditions, concentration of Fe(III) ion in the ferric carboxylates and the chain length of the alkyl part of the added prodegradants play an important role in the rate of PP photodegradation. The PP material degraded faster as expected in the summer season due to the higher average outdoor temperature even though average UV and visible light intensity were low when compared to winter season (TABLE 1). This result clearly indicated that the average outdoor temperature influences more on the PP photodegradation while all other weather parameters also participate considerably in the PP degradation. Further, the results showed that as the number of carbon atoms in the alkyl part of the prodegradants increases the time necessary to reach particular hydroperoxide index value also increases. The probable explanation for this observation is that as the length of alkyl radical formed from the prodegradants increases, the mobility of the radical in the PP matrix is reduced and hence the rate of degradation reaction decreases.

Broska and Rychly followed the build-up of hydroperoxide by direct FTIR measurement and the absorbance at 3420 cm<sup>-1</sup> is attributed to the adjacent hydroperoxides. The authors revealed that during ageing, the concentration of hydroperoxide reached a maximum and then it decreased. In contrast, Valadez-Gonzalez et al. and Luzuriaga et al. showed that on thermal ageing, there was a gradual increase in the hydroperoxide concentration. In PP higher hydroperoxide concentration was expected due to the structural factors which favour the chain scission. A similar gradual increasing trend was observed in this present investigation.

### ***Crystallinity Index***

Crystallinity index was calculated as the ratio of absorbance of band at 998 cm<sup>-1</sup> to the absorbance of band at 974 cm<sup>-1</sup> in order to gather information on the variation of crystallinity as the function of days of exposure. The first band is regularity band characteristic of the crystalline PP, whereas the second band corresponds to both crystalline and amorphous PP phases. The results showed that as the photodegradation of PP progressed, the crystallinity index increased after certain exposure days where the indices of hydroperoxide, hydroxyl, carbonyl, lactone, ester and carboxylic acid increased. This may be due to

the fact that the formation of new low molecular weight photooxidation products like hydroperoxide, hydroxyl, carbonyl, lactone, ester, carboxylic acid, etc., are capable of forming new crystalline domains.

Yakimets et al. reported the crystallinity variations in photooxidized PP and the variations were investigated using FTIR, X-ray diffraction and DSC techniques. The authors showed that the crystallinity fraction increased when a sudden drop of the strain at failure and the molecular weight decreased drastically. The authors have given explanation for this observation that the photooxidation causes molecular chain scissions in the amorphous regions and these parts of cut chains rearrange into a crystalline phase and hence the decreases in molecular weight and the fall of mechanical properties are related to the increase of the crystallinity fraction.

## **Mechanical Properties Measurements**

### ***Elongation at Break***

The elongation at break percentages was calculated using force *versus* elongation curves and its variations as a function of days of exposure are depicted in FIG. 7A. Virgin PP when exposed to natural weathering conditions in winter and summer seasons, the elongation at break percentages showed no conspicuous changes upto 45 day and 40 day respectively. Sudden decrease to near zero value for the elongation at break percentage is noted indicating the occurrence of main chain scissions in PP. This behaviour may be attributed to the presence of stabilizers in the commercial grades of PP, which have a role to protect the polymer against degradation during outdoor weathering. Another possible explanation for this observation is that during the photooxidative degradation of PP, exclusive morphological changes without any chemical changes in the PP are occurring during the initial phases of degradation. But, in the case of PP containing prodegradants, the loss of the elongation properties happens at around 15 day and 10 day of exposure to natural weathering in winter and summer seasons respectively and thus rendering the films unserviceable for practical applications.

Further, from the FIG. 7A, the order of this loss of elongation at break (%) was observed as: MF03 > MF04 > MF05 > MF06 > MF07. This result indicated that as the

number of carbon atoms in the alkyl part of the prodegradants increased, the time necessary for the main chain scission increased. So, the mobility of the alkyl radical in the polypropylene matrix which is undergoing natural weathering is an important factor which governs the rate of UV induced photooxidative degradation.

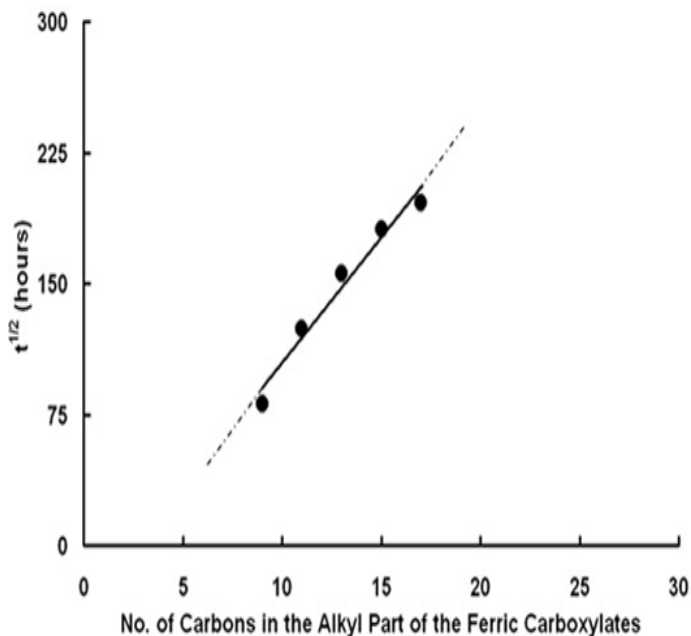


FIG. 8 A PLOT OF HALF-LIFE *VERSUS* NUMBER OF CARBON ATOMS PRESENT IN THE ALKYL PART OF THE FERRIC CARBOXYLATES FOR NATURALLY WEATHERED PP CONTAINING 0.2% OF FERRIC CARBOXYLATES FOR SUMMER SEASON.

The time needed for the material to lose 50 % of elongation at break percentage from its initial value has been taken as  $t_{1/2}$ . A plot of  $t_{1/2}$  versus number of carbon atoms present in the alkyl part of the added prodegradants (FIG. 8) gives a straight line. The results thus showed that the rate of UV induced photooxidative degradation of PP is linearly related to the number of carbon atoms present in the alkyl part of the added prodegradant, ferric carboxylate. This result can also be correlated with concentration of Fe(III) ion in the ferric carboxylates added to the PP and showed that the  $t_{1/2}$  time decreased gradually and almost linearly with an increase of concentration of ferric ion in the ferric carboxylates blended with PP (FIG. 9). This may be due to the fact that the tendency of absorption of light radiation by the PP material containing ferric carboxylates increases with increase in the concentration of Fe(III). As a result it produces more number of alkyl radicals easily and accelerate the PP degradation.

### Tensile Strength

It is an important measure of product quality to certify the product and therefore its variation during weathering is to be followed to judge the degradation. The variation of tensile strength of virgin PP and PP containing different prodegradants during natural weathering at summer season are shown in FIG. 7B. Almost in all cases, PP films and PP films containing prodegradants, tensile strength decreased gradually at the initial stages of weathering and then tensile strength decreased rapidly.

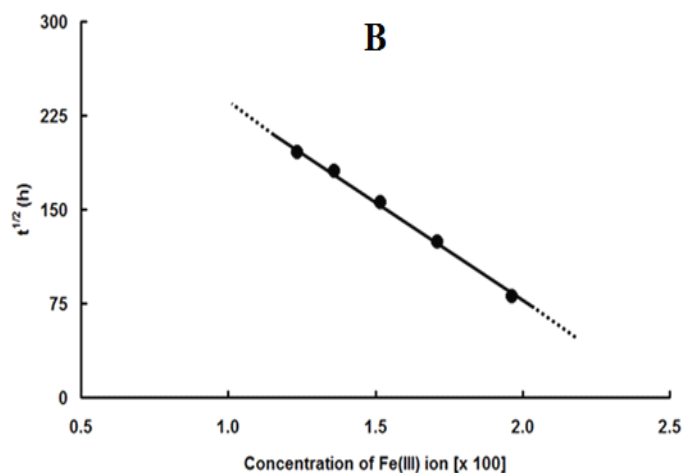
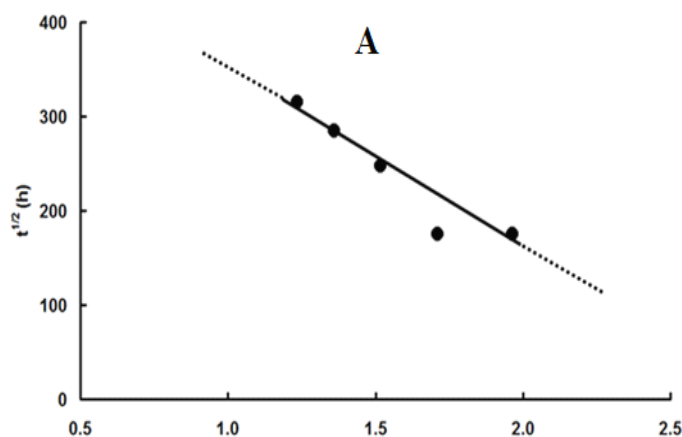


FIG. 9 A PLOT OF HALF-LIFE *VERSUS* CONCENTRATION OF FE(III) ION IN THE FERRIC CARBOXYLATES FOR NATURALLY WEATHERED PP CONTAINING 0.2% OF FERRIC CARBOXYLATES: (a) WINTER AND (b) SUMMER SEASON.

This behaviour is explained due to the chain reorganization phenomenon and lower degree of orientation that is present in PP. All the materials investigated (PP virgin and PP containing prodegradants) retain 20-40 % of their tensile strength. Further, a rapid decrease of tensile strength value appeared only at the time of a steep increase of

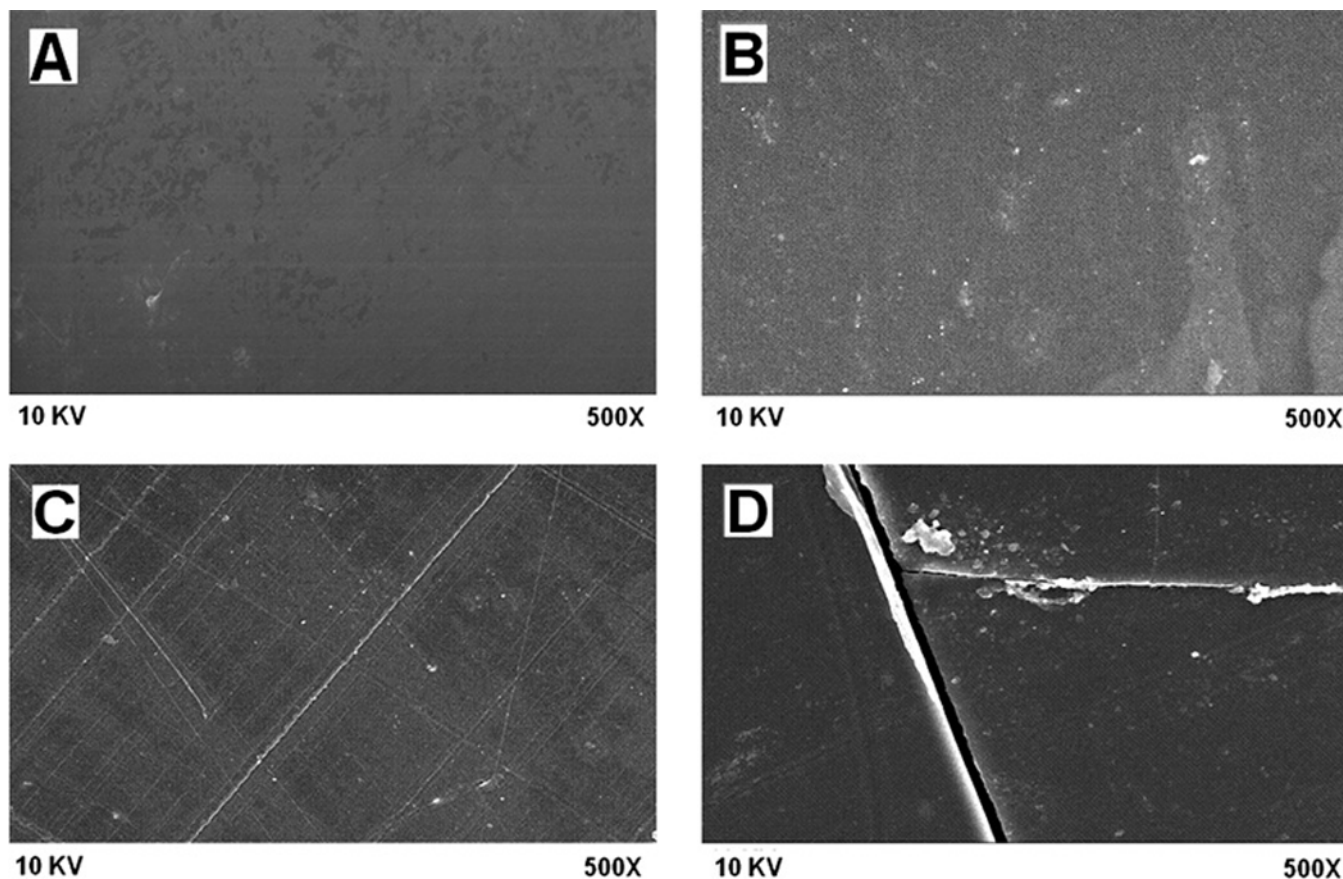


FIG. 10 SEM IMAGES: (A) VIRGIN PP, (B) NON-WEATHERED PP:MF07, (C) 9 DAY WEATHERED PP:MF07 AND (D) 13 DAY WEATHERED PP:MF07.

carbonyl index value (FIG. 7B) and this behavior of weathered virgin PP was also shown by Gallo et al. during natural weathering of PP at Messina, Italy.

### SEM Characterisation

The dispersibility of the iron carboxylates in PP and surface morphology changes of PP material during weathering were characterized using scanning electron microscope. The SEM image of virgin PP (FIG. 10A) indicates a smooth surface without any cracks while in FIG. 10(B), a few numbers of white spots are seen and which may be the iron carboxylates particles spread randomly in the PP matrix. The SEM image of six days weathered PP:MF03 (FIG. 10(C)) shows regions wherein the cracks are developed. Cracks and grooves appeared in the 9 day weathered PP:MF03 (FIG. 10(D)) and is due to the main chain scission in PP which reflects in the steep increase of the indices of carbonyl, hydroperoxide, lactone, ester, and carboxylic acid and a sudden decrease of elongation at break percentages and tensile strength.

From the foregoing investigations, the authors prefer ferric stearate for detailed investigations. Ferric carboxylates are non toxic. Stearic acid and stearates are

generally used in the processing of thermoplastic polymers as processing aid preferably as lubricants. Hence, ferric stearate can be safely used as a prodegradant in poly olefins.

### Conclusions

The scission of the main chain of the polypropylene due to the effect of added prodegradants ferric carboxylates and the natural weathering conditions at summer season is established from the steep increase of carbonyl, hydroperoxide, lactone, ester, and carboxylic acid indices and a sudden decrease of elongation at break percentages and tensile strength and development of surface cracks. The effectiveness of the prodegradants on the photodegradation of PP is in the order ferric caprate > ferric laurate > ferric myristate > ferric palmitate > ferric stearate. The results showed that the PP and PP containing 0.2% of ferric carboxylates degraded faster as expected in the summer season than that in the winter season. This effect is being controlled and influenced by the average weathering parameters mainly outdoor temperature. Moreover, the curves of all carbonyl index regions showed almost a gradual parallel shift indicating PP, whether it is virgin PP or



prodegradant blended PP, degraded without much change in the degradation mechanism. The steep increase of the carbonyl and hydroperoxide indices occurring in the same time span during natural weathering showed the unstable hydroperoxide formation and its decomposition leading to carbonyl groups are occurring simultaneously during the photodegradation of virgin PP and PP containing ferric carboxylate. From the plot of  $t_{1/2}$  versus number of carbon atoms presented in the alkyl part of the added prodegradants, it is concluded that as the number of carbon atoms in the alkyl part of the fatty acid part in the ferric carboxylate increased, the rate of UV induced photooxidative degradation decreased and the effect is found to be linear. Finally, the authors concluded that the interplay of the ease of formation of the alkyl radical from the ferric carboxylate, the stability of the produced alkyl radical, its mobility in the weathering polypropylene matrix and the concentration of Fe(III) ion introduced in PP films are the parameters which determine the rate of the photodegradation of polypropylene. The authors planned to study further the efficiency of ferric stearate as prodegradant for the photooxidative degradation of both low density and high density polyethylenes since these materials are also extensively used for packaging apart from polypropylene.

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